

Evaluation of Solvent Alternatives for Cleaning of Oxygen Systems

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The NASA White Sands Test Facility (WSTF) in a joint program with the Naval Sea Systems Command has evaluated a number of solvents as alternatives to the use of chlorofluorocarbons currently utilized for cleaning of oxygen systems. Particular attention has been given to the cleaning of gauges and instrumentation used in oxygen service, since there have been no identified aqueous alternatives. The requirements identified as selection criteria, include toxicity, physical properties consistent with application, flammability, oxygen compatibility, and cleaning ability. This paper provides a summary of results and recommendations for solvents evaluated to date.

ALTERNATIVE SOLVENTS

While many evaluations of alternative aqueous processes have been carried out, a need still exists for nonaqueous solvents. A recent investigation by the Navy has identified the cleaning and verification of high-pressure gauges and precision instrumentation as one area for which no aqueous alternative exists and for which an alternative must be identified (Antin 1994). As part of an effort sponsored by NAVSEA, several alternative solvents were examined. Solvent properties considered in the cleaning of gauges and instrumentation include:

- The ability to remove contaminants
- The ability of the solvent to be removed from the cleaned part
- The solvent's flammability characteristics, which are crucial for solvents to be used in oxygen systems
- The solvent toxicity
- The ability of the solvent to be used as a verification fluid

The solvents that have been investigated to date represent a wide range of chemistries and include a chlorinated hydrocarbon, an alcohol, a perchlorinated alkene, an ether, hydrochlorofluorocarbons, hydrofluorocarbons, and hydrofluoroethers. In addition, CFC 113 was submitted for comparative purposes. The solvents studied and their physical properties are listed in Table 1. Tert-butylmethylether and n-Hexane were evaluated in early testing but were not considered for further testing because of combined concerns related to toxicity and flammability. In addition not all solvents tested for oxygen compatibility were evaluated for cleaning effectiveness, particularly if the solvent showed gross incompatibility with oxygen.

Table 1. Solvents Studied and their Physical Properties

Solvent	Boiling Point (°C)	Threshold Limit Value (ppm)	Flammability
PCE	121	25 ^a	No
TCE	87	50 ^a	Yes
Ethanol	78	1000 ^a	Yes
AK 225 [®]	53	50 ^b	No
HCFC 141b	32	500	Yes ^c
HFE 7100 [®]	60	600 ^b	No
Vertrel MCA [®]	39	200 ^b	No ^d
Vertrel XF [®]	48	200 ^b	No
HFE 71DE [®]	41	200 ^b	No ^d
OS-10 [®]	100	200 ^b	Yes
ABZOL [®]	71	100 ^b	Yes ^c
EnSolve [®]	69	100 ^b	Yes ^c
CFC 113	48	1000 ^a	No

^a *Guide to Occupational Exposure Values*, American Conference of Governmental Industrial Hygienists, 1994.

^b TLV data provided by manufacturer.

^c Flammability limits have been established, but Material does not have a flash point.

^d Flammability of the mixture has not been determined, and it has no flash point.

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The solvents were evaluated using a variety of gauges and instrumentation types including closed- and open-ended, high- and low-pressure, Bourdon tube-type gauges. This type of gauge was selected because it presents the greatest challenge to a cleaning solvent. The solvents were evaluated according to their ability to remove a variety of commonly encountered contaminants including Krytox 240AC, the hydraulic fluids Mil-H-5606 and Mil-H-83282, and the gauge calibration fluids Spinestic 22 and Sebacate. The gauges were contaminated with a known amount of contaminant before cleaning.

In general, the gauge was cleaned using five solvent volumes. Closed-end tubes were filled with solvent and then evacuated and purged to remove the solvent using a cleaning panel designed so that the maximum pressure used to fill the gauge was 35 psi (238 kPa). Open-ended gauges were rinsed with five 100-mL volumes of the solvent. In both cases, the final volume of solvent was collected, and the nonvolatile residue (NVR) was determined. The solvent removal was expressed as a percentage of contaminant removed.

The efficiency of these solvents in removing selected contaminants from Bourdon tubes in either closed or open configurations is given in Table 2. Nearly complete contaminant removal was shown by HCFC 225 and CFC 113 in both open- and closed-tube configurations. All solvents showed acceptable contaminant removal for the open-tube configuration. As expected, the greatest range came from the closed-tube configuration. The performance of HFE 7100 is of note because a lower contaminant removal efficiency was expected based on vapor degreasing operations. The greater-than-expected performance is because of the physical action of the gauge-cleaning process, which adds to the inherent contaminant-removal ability of the neat solvent. This may be of importance to other cleaning operations in which solvents are used to flush components where mechanical action is present and the HFE 7100 would be expected to perform well. Also of note is the increased cleaning efficiency that is obtained when the neat solvent is blended with 1,2-Dichloroethylene (DCE), compare Vertrel XF with Vertrel MCA and HFE 7100

with HFE 71DE. The addition of DCE increases the solvent efficiency by 10 to 20 percent; however the DCE may increase the toxicity of the solvent and increases the flammability of the solvent in an oxygen system(see below).

Table 2. Average Solvent Cleaning Efficiencies

Solvent	CE Gauges	OE Gauges	Average
Tetrachloroethylene	74	97	87
Ethanol	82	86	85
Trichloroethylene	84	98	92
AK 225	100	98	99
HCFC 141b	96	98	97
HFE 71DE	99	98	98
HFE 7100	93	91	92
Vertrel MCA	98	98	98
Vertrel XF	80	88	84
AK-225S	96	96	96
CFC 113	99	95	97

Flammability is an issue with nonhalogenated organic solvents used for cleaning parts; alcohols, ketones, and ethers can be extremely flammable. In the case of cleaning parts for oxygen, oxidizer, and high-pressure air service, if the solvent is not completely removed from the part or is absorbed into softgoods, the part may ignite during operation. Flammability is not only a concern for organic solvents but also for some chlorinated and fluorinated solvents that contain hydrogen. In many instances flammability has been evaluated based on results obtained in air; however, oxygen enriched environments are known to increase the flammability of materials including rendering solvents, which would in air be considered nonflammable, flammable.

The AIT and Ambient Pressure Liquid Oxygen (LOX) Impact Sensitivity was determined for the test solvents according to the procedures described in ASTM G-72 and ASTM D 2512, respectively. The AIT for each solvent was determined at 50 and 2000 psig and the purge procedure was modified so that the solvents would not evaporate during the purge. The LOX impact testing was accomplished using a stainless steel insert and the standard grease cup which provides a solvent thickness of .050 inch under the impact striker pin and provides maximum confinement of the sample during the impact event. The results for all the solvents tested are given in Table 3, while specific test results for HCFC 141b are given in Table 4. In all tests the neat solvent was tested and not panels which had been rinsed with the solvent and allowed to dry since this procedure only test the panels reactivity in oxygen and not the solvent's.

An AIT was observed for PCE, TCE, Vertrel MCA, Vetrel XF, HFE 7200, HFE 71DE, OS-10, ABZOL, and EnSolve, while HCFC 225 and HFE 7100 did not ignite under the test conditions. The ignition behavior of HCFC 141b was dependent on the amount of NVR carried by the solvent, whereas at NVR below 17 ppm no ignitions were observed; however, at higher NVR an AIT was measured (Table 4). The AIT recorded for TCE is low compared to other compounds typically considered oxygen compatible. The AIT determined for solvents that contain DCE seems to be associated with the DCE itself since the AITs are all within the same range for the data presented. A slow temperature rise for PCE and TCE was observed during the 50 -psig test, indicating that both compounds burned slowly or gave off little heat at that pressure.

Table 3. AIT Results for Solvents Tested

Solvent	AIT	AIT	LOX Impact ¹
	@50 psi (°C)	@2000 psi (°C)	
CFC 113	NI	NI	NO
Tetrachloroethylene	136	161	NO
Trichloroethylene	108	77	NO
HFE 71DE	NI	157	YES
Vertrel MCA	NI	167	NO
HFE 7100	NI	NI	NO
Vertrel XF	NI	241	NO
HCFC 141b ²	NI	NI	NO
HFE 7200	NI	262	NO
OS-10	125	224	Yes
ABZOL VG & EnSolve	102	185	Yes
HCFC 225	NI	NI	NO

NI = No Ignition (did not ignite at maximum test temperature of 450 °C)

¹ Reactions in Mechanical Impact at 72 ft lbs

² Nonvolatile residue of solvent was less than 17 ppm.

Table 4. HCFC 141b Oxygen Compatibility Test Compared to NVR

NVR (ppm)	AIT @ 50 psig & @ 2000 psig	Mechanical Impact 98 J or 72 ft-lb	
		Ignition	
28	Exotherm ^a	Ignition	6/38 ^b
20	NR ^c	Passed	1/60
17	NR	Passed	0/20
3	NR	Passed	NR

^a Two mild exotherms were observed at 261 and 321 °C.

^b 6/38 ignitions: 3 @ 72 ft-lb, 1 @ 65 ft-lb, 1 @ 60 ft-lb, and 1 @ 55 ft-lb.

^c A mild exotherm was observed at 2000 psig at 47 °C.

NR = No reaction

The solvents were also tested for ignition by mechanical impact at ambient pressure in liquid oxygen according to the procedures described in ASTM D-2512. HCFC 141b, HFE 71DE, OS-10, ABZOL, and EnSolve reacted in mechanical impact. For HCFC 141b, the mechanical impact sensitivity was again a function of the amount of NVR contained in the solvent; so long as the NVR level was kept below 17 ppm, the solvent did not react in mechanical impact. HFE 71DE also contained a high level of NVR due to the DCE and it is felt that this contributed to its impact sensitivity. Testing with an early formulation of Vertrel XF with DCE and nitromethane stabilizer was also reactive in mechanical impact at energy levels from 72 to 20 ft-lb. However, the reactivity seems to be a function of the nitromethane stabilizer that was present in a concentration of 0.3 to 0.9 percent. When the Vertrel MCA was tested, which does not contain nitromethane, it did not react at an energy of 72 ft-lb. The removal of nitromethane from other solvent formulations i.e. ABZOL and EnSolve; however, did not change the reactivity with oxygen.

To decrease the hazards associated with the use of solvents in oxygen systems, the reactivity of the solvent in the environment must be considered. A solvent that is reactive in the environment should not be used unless it can be shown that the solvents complete removal can be assured. This would limit some of the solvents tested application in the cleaning of assembled components or complex geometries. In particular for the cleaning of high pressure gauges, which represents a severe oxygen service since these gauges are routinely rapidly pressurized and are a dead-ended component, the use of a flammable solvent should be approached with caution and the processes engineered so that the hazard is minimized. For liquid oxygen systems a solvent that is impact sensitive should again not be used unless the solvent is carefully removed since LOX will not allow for solvent evaporation and will tend to concentrate contaminants even those present in the vapor phase at ambient temperature.

SUMMARY

To date, a series of twelve solvents has been tested to determine their effectiveness in cleaning of high-pressure gauges and instrumentation and for their compatibility with liquid and gaseous oxygen. All of the solvents tested exhibited adequate cleaning ability in this application, with toxicity and flammability as the major discriminators for the selection of fluids. Great care should be taken in the selection of solvents for cleaning of oxygen systems, and flammable solvents such as alcohols should only be used under the strictest of controls. Testing is being continued on solvents, as they become available.

REFERENCES

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